Martian Oxidant: may be ferrate Fe(VI)?

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Fe(VI) in the form of ferrate salts, with FeO_4^{2-} anion, was studied for its spectral and oxidative properties, with the question of whether it might be a suitable analog of the Mars soil oxidant, proposed as a result of the Viking missions of the early 1970s. Ferrate(VI) has distinctive spectroscopic features that make it available for detection by remote sensing reflectance spectra and contact measurements *via* Mössbauer spectroscopy, and the relevant miniaturized instrumentation have been developed or is underway, while for returned sample XANES spectroscopy is a method of choice. Ferrate(VI) is capable of splitting water to yield molecular oxygen, and oxidizing organic carbon into CO_2. These activities were strongly abated after treatment at elevated temperatures, similar to observations with Mars soil samples in Viking mission.

Since the Viking missions of the 1970's, the existence of life on the surface of Mars has been strongly doubted, and indeed, even organic matter, which should have been delivered to the planetary surface via meteorites and comets, appeared to not be present[1,2,3]. The Viking biology experiments revealed however an unexpected chemical activity in the surface material: 1) moisturizing Martian soil resulted in oxygen evolution; 2) addition of a ^{14}C-labelled nutrient solution (formate, glycine, lactate, alanine, and glycolate) resulted in [14]CO_2 evolution in the reaction chamber; and, 3) "sterilization" (i.e. pre-heating of soil samples at 160°C) inhibited carbon dioxide release almost completely, while oxygen evolution was only partially reduced by pre-heating. These observations were interpreted as indications on the presence of a strong oxidant, or more likely, several different kinds of oxidants on the Martian surface[1,4]. Such oxidant(s) would be incompatible with organic matter, thus making unlikely the presence of life on the Martian surface.

For future Mars exploration, it would be helpful to understand the nature the Mars oxidant(s), and indeed, considerable effort (primarily in laboratory studies) has gone into the search for oxidants that can mimic the Viking results. Several oxidants have been considered, but to date, none has emerged with the appropriate properties. Among candidates that have been proposed so far, were hydrogen peroxide and other active oxygen species, such as superoxide which çan be formed due to the UV irradiation of Martian soil[5,6,7,8,9]. Recently, it was shown that TiO_2 adsorbs hydrogen peroxide on its surface, and the resulting system can mimic Viking experiments in laboratory conditions fairy well[10]. Such a sorption is actually accompanied with at least partial chemical transformation of the material, as revealed, e.g., by formation of stabilized, EPR-active products, including, most likely superoxide radical anion[11].

One potential oxidant that appears to has not been considered so far is Fe(VI). Such an opportunity should *not* be ignored, especially taking into consideration that iron is one of the most abundant elements on Mars surface: 19 mass percent, on metal oxide basis, while, e.g.,
titanium dioxide has an estimated abundance of 0.6 mass percent only[12]. Under certain conditions, higher oxidation states of iron [Fe(IV), Fe(V), and Fe(VI)] can be formed[13].However, while Fe (IV) and Fe (V) are extremely unstable, and rapidly decompose into Fe(III) and Fe(VI), iron(VI), in the form of ferrate [FeO_4^{2-}] salts,

even though an extremely strong oxidant, is rather stable in alkaline solutions, and as a dry salt with several cations.

Formation of ferrate(VI) as a purple by-product in some strongly alkaline solutions, was first described as early as 1702[14]. Later, ferrates(VI) with various cations, such as potassium, sodium, barium, lithium, rubidium, cesium, silver(I) and even some tetra-alkyl/aryl ammonium salts, have been described[15,16,17,18]. The most thoroughly characterized species, potassium ferrate, K_2FeO_4, has been prepared as dark purple crystals, decomposing at *ca.* 200°C with oxygen release[15]. More recently, there has been interest in ferrate as an oxidizing agent for organic synthesis[16,19], and material for rechargeable alkaline batteries of high capacity[20]. Here we present data on spectral characterization and chemical activities of potassium ferrate, and make the case that this oxidant should be measured in upcoming Mars experiments.

Several procedures were previously suggested to prepare ferrate(VI): electrochemical oxidation of iron anode[21], calcination of a mixture of ferric oxide with potassium peroxide in the stream of oxygen[23], and wet oxidation of Fe(III) to Fe(VI) by hypochlorite or hypobromite in a highly basic solution[15,16]. The last approach seems most practical for preparation purposes, and was applied in these experiments. Crystalline potassium ferrate was prepared by the wet procedure, essentially as outlined in ref. 16. First, concentrated solution of potassium hypochlorite, KClO, was formed by bubbling chlorine gas into cold 10M KOH. Iron(III) nitrate was added in small portions to hypochlorite solution, resulting in the formation of dark purple ferrate. Solid potassium hydroxide was added to this purple solution, precipitating potassium ferrate(VI), which was then separated by vacuum filtration through a coarse glass filter. Black crystals thus produced were washed with few portions of cold hexane and diethyl ether to remove traces of water. The stability of the product critically depends on water removal. It was kept in dessicator over KOH pellets. Barium ferrate was prepared in an essentially same way, except that commercial bleach (sodium hypochlorite solution) was applied instead of potassium hypochlorite, and barium oxide was added at last stage instead of potassium hydroxide. Red crystalline $BaFeO_4$ is very low soluble, and more stable in the presence of moisture compared to K_2FeO_4.

Potassium ferrate(VI) is stable in alkaline solutions, exhibiting a deep purple color due to the tetrahedral FeO_4^{2-} dianion, with its absorption peak at 507-510 nm. The strong absorption at this wavelength (ε =1100-1300 M^{-1}cm^{-1}) makes Fe(VI) easy to distinguish from other various oxidation states of iron. A characteristic band at 1.6 μm was found in its reflectance spectra (Fig. 1a), suitable for remote sensing on Mars surface from an orbiter apparatus.

In contact measurements, most promising approach to the identification of oxidation states of iron is provided by Mössbauer spectrscopy. It is especially important in the context of these studies since a compact Mössbauer instrument has been developed for the analysis of the Martian surface in forthcoming Mars missions[24]. The room temperature Mössbauer spectrum of a sample containing K_2FeO_4 together with other iron species (Fig. 1b), reveals a singlet component that exhibits a negative isomer shift (opposite in sign to the isomer shifts for Fe(II) and Fe(III) phases). This was identified as the primary Fe(VI) phase and its isomer shift is slightly more negative than previously reported for this compound in ref. 26. A negligible quadrupole splitting is expected for Fe(VI) in K_2FeO_4 based on its $3d^2$ electronic configuration in a tetrahedrally coordinated site. When samples contained a mixture of Fe(VI) and Fe(III), another, doublet component was seen in Mössbuaer spectrum, with an isomer shift and quadropole splitting consistent with a paramagnetic Fe(III)-bearing phase. It is important that Mössbauer spectroscopy permits to identify Fe(VI) even as a small admixture to Fe_2O_3 phases which are expected to be more abundant.

Ferrate(VI), with its sd^3 hybridized iron and two unpaired 3d electrons, is paramagnetic and EPR active[27]. Non-oriented powder samples of potassium ferrate display a singlet EPR spectrum at g=1.998, with line-width of ca.

8 mT at 77 K. This signal is significantly broadened at room temperature (Fig. 1c). Again, a miniature EPR instrument have been developed for future Mars expeditions[28].

Though returning samples analysis is an issue of a more remote perspective, we explored here the opportunity of identifying Fe(VI) phase in such samples using X-ray absorption near edge spectra (XANES, Fig. 1d). In this technique, the focus is on the region very close (within about 30eV) to the ionization threshold of the compound in question. The structure of the absorption spectrum there is very sensitive to the three-dimensional geometry of the atoms surrounding the excited atom (i.e. iron). Comparison of XANES spectra of a sample with XANES spectra of known standards allows identification of the oxidation state of, and local geometry around iron, for which X-ray absorption edge energy is ~7112 eV. Characteristic pre-edge feature is observed from both solutions and solid samples containing tetrahedrally coordinated Fe(VI) in ferrate(VI) dianion. Sensitivity is about 10 ppm, in the presence of other states of iron, which makes XANES a method of choice for the analysis of returning samples.

Reactions with water and aqueous solutions. Addition of water to potassium ferrate(VI) results in immediate and intensive gas evolution (bubbling). GC-MS analysis of gas product after this reaction with $H_2^{18}O$ revealed that the gas product is dioxygen (data not shown). The presence of $^{18}O_2$ in head space of reactor vessels indicated that Fe(VI) can oxidize water with oxygen evolution while no essential oxygen exchange takes place between ferrate(VI) anions and water.

Oxidation of organic carbon was explored using formate and lactate as substrates. Addition of an excess of aqueous solutions of these organic acids to crystalline potassium ferrate(VI) resulted in concomitant evolution of both oxygen and carbon dioxide in the head space of reactor vessels (Fig. 1e, f). Both water and organic carbon oxidations are functions of pH of solutions reacting with solid ferrate(VI), and of their buffer capacities. In addition, solubility of gases, especially that of CO_2, also depends on pH this complicating observations. . Therefore the net relative amount of each of the gases measured with this method may vary.

Thermogravimetric analysis and differential scanning calorimetry (data not shown) both show that potassium ferrate(VI) is quite sensitive to heating, and its thermal decomposition is a multistep process starting at a temperature only slightly over 50°C and completed at about 300°. Most probably, lower oxidation states of iron such as Fe(IV) and (V) appear as transient species, before Fe(III) is eventually formed. Accordingly, preheating of potassium ferrate(VI) decreased or prevented subsequent oxidation of both water and organic carbon. For instance, in these experiments, preheating for 4 hrs at 105°C suppressed further CO_2 production from formate by about 30 percent, while preheating at 160° C resulted in 75 percent inhibition.

The possibility of ferrate(VI) formation and preservation in Martian soil should be addressed. In neutral and acidic solutions ferrate is quite unstable, with its standard potential of about 2.20V, as reported earlier[29] for the equilibrium $FeO_4^{2-} + 8H^+ + 3e^- \Leftrightarrow Fe^{3+} + 4H_2O$, so that both water and organic compounds are oxidized. Standard potential decreased down to 0.72 V in strongly alkaline solutions, for the equilibrium $FeO_4^{2-} + 4 H_2O + 3e^- \Leftrightarrow Fe(OH)_3(s) + 5OH^-$. Therefore, one would need a highly alkaline liquid environment for ferrate(VI) to be formed and stored, and some strong oxidants all around.

Such conditions might have existed on ancient Mars, or during the period in which the climate changed to what it is today. Indeed, there are various reasons to assume that in the absence of calcium carbonate biogenic deposits which now serve as a powerful buffer on Earth surface, both pre-Cambrian Earth and Mars at some stage of its geological history were covered with "soda ocean" with pH>9 [30,31]. The UV flux on Martian surface can generate oxygen radicals of high oxidative power, which would interact with Fe(III) so abundant on Martian surface, thus producing Fe(VI). Formation of Fe(VI) by reactions with peroxides was previously documented[22].

Given that the Martian surface is now cold and dry, even alkaline ferrates would persist there, while ferrates(VI) of some other metals are generally more stable. Therefore, there is enough reason to suggest that the accumulation of ferrate(VI) in Martian soil is possible.

So what about ferrate as a candidate for the martial oxidant? It mimics the Mars oxidant in several important ways: 1) it induces oxygen evolution after contact with water; 2) it oxidizes organic material with the release of CO_2; 3) These activities of ferrate can be observed simultaneously and concomitantly, and both are sensitive to preheating, though not in the same way. All these properties are in accordance with the observations made by Viking lander. Therefore, we conclude that ferrate(VI) is a good candidate to put forward as a potential Mars oxidant. Probably not the only one, but perhaps one of a mixture that combine to have the effects noted in Viking expedition. A strong feature of this hypothesis is that it is possible to test it. The upcoming Mars 2001 will have the capability to measure reflectance spectra samples *in situ*. Even more decisive data will be collected with Mössbauer spectrometer which is a part of Athena payload. As we mentioned above Mössbauer spectra of Fe(VI) can provide a definite answer on the presence of Fe(VI) in Martian soil.

References

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Captions

Fig. 1   a: Reflectance spectra of potassium ferrate(VI) (1), and its
mixtures with CaO (2), and CaO+Fe_2O_3 (3).

    b: Mössbauer spectrum of a sample containing potassium
ferrate(VI) and Fe_2O_3. (Ranger Scientific constant acceleration spectrometer with 1024-channel
pulse height analyzer).

    c: EPR spectrum of potassium ferrate(VI) powder at 77 K and room temperature (Bruker ESP-300
instrument).

    d. X-Ray absorption near edge spectra (XANES) of K_2FeO_4 (1), $Fe(NO_3)_3$ (2), and $FeCl_2$ solutions.
(Obtained using the Advanced Photon Source facility, Argonne National Laboratory).

    e: Oxygen evolution at potassium ferrate(VI) reaction with pure water. pH effect on O_2 and
CO_2 evolution in the reaction of ferrate(VI) with 0.1M formate (simultaneous measurements with
two sensors).

    f. CO_2 release in the reaction of potassium ferrate(VI) with formate: Effect of preheating 4 hrs at
105 (2) or 160°C (3). [in e) & f) measurements with Columbus Instruments Micro-Oxymax
close-circuit respirometer]

a

10

70

10

1.200   1.700   2.200
wavelength, nm

b

0

-2

-4

-6

-8

-10

Absorption [%]

-8 -6 -4 -2 0 2 4 6 8 10
Source Velocity [mm/s]

c

300 K   77 K

dχ″/dH

0.25   0.30   0.35 T

d

Step Height Normalized Data (I/I_0)

2

1.5

1

0.5

0

—— Fe(6+) Solution
－ － Fe(3+) Solution
····· Fe(2+) Solution

-20   0   20   40   60   80   100
Energy Relative to Fe foil (E_0=7112 eV)

e

Oxygen Evolution, μL/mg

50
45
40
35
30
25
20
15
10
5
0

0 10 20 30 40 50 60 70
Time, min

pH Effect on oxygen(1) and carbon dioxide(2) evolution

1
0.8
0.6
0.4
0.2
0

2   4   6   8
pH

μL/mg

2

1

f

Carbon dioxide release, μL/mg

140
120
100
80
60
40
20
0

Carbon dioxide, μL/mg

1

2

3

0   20   40   60   80
Time, min